Communication

A Super-Oxidized Radical Cationic Icosahedral Boron Cluster

Julia M Stauber, Josef Schwan, Xinglong Zhang, Jonathan Axtell, Dahee Jung, Brendon James McNicholas, Paul H. Oyala, Andrew J. Martinolich, Jay R. Winkler, Kimberly A. See, Thomas Francis Miller, Harry B. Gray, and Alexander M Spokoyny

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.0c06159 • Publication Date (Web): 09 Jul 2020

A Super-Oxidized Radical Cationic Icosahedral Boron Cluster

Julia M. Stauber, Josef Schwan, Xinglong Zhang, Jonathan C. Axtell, Dahee Jung, Brendon J. McNicholas, Paul H. Oyala, Andrew J. Martinolich, Jay R. Winkler, Kimberly A. See, Thomas F. Miller III,* Harry B. Gray,* Alexander M. Spokoyny*

ABSTRACT: While the icosahedral *closo*-$[B_{12}H_{12}]^{2-}$ cluster does not display reversible electrochemical behavior, perfunctionalization of this species *via* substitution of all twelve B–H vertices with alkoxy or benzyloxy (OR) substituents engenders reversible redox chemistry, providing access to clusters in the dianionic, monoanionic, and neutral forms. Here, we evaluated the electrochemical behavior of the electron-rich B_{12}(O-3-methylbutyl)$_{12}$ (**1**) cluster and discovered that a new reversible redox event that gives rise to a fourth electronic state is accessible through one-electron oxidation of the neutral species. Chemical oxidation of **1** with $[N(2,4\text{-}Br_2C_6H_3)_3]^{\bullet+}$ afforded the isolable $[\mathbf{1}]^{\bullet+}$ cluster, which is the first example of an open-shell cationic B_{12} cluster in which the unpaired electron is proposed to be delocalized throughout the boron cluster core. The oxidation of **1** is also chemically reversible, where treatment of $[\mathbf{1}]^{\bullet+}$ with ferrocene resulted in its reduction back to **1**. The identity of $[\mathbf{1}]^{\bullet+}$ is supported by EPR, UV-vis, multinuclear NMR (^{1}H, ^{11}B), and X-ray photoelectron spectroscopic characterization.

Polyhedral boron clusters have provided a platform for rich scientific exploration with applications ranging from materials science to medicine.[1–10] The icosahedral *closo*-$[B_{12}H_{12}]^{2-}$ dianion[11] has been a focus of investigation on account of its high stability, three-dimensional delocalized bonding, resistance to harsh chemical environments, and ease of electrophilic B–H substitution.[12] Work describing the one-electron oxidation of $[B_{12}H_{12}]^{2-}$, however, displayed cluster decomposition and dimerization, revealing the oxidative instability of this species.[13] These findings were rationalized by the Wade-Mingos $2n + 2$ (n = number of vertices) electron-counting rules, which predict the structures of polyhedral molecules based on the number of skeletal electron pairs (Figure 1A).[14,15] However, despite these predictions, perfunctionalization of *closo*-$[B_{12}H_{12}]^{2-}$ can engender reversible redox chemistry, which provides ready access to neutral, *hypercloso*-$B_{12}R_{12}$ derivatives (Figure 1B).[12,16–20] Stabilization of these species is attributed to steric protection of the cluster-confined frontier orbitals by bulky substituents, and the electron-donor effects of supporting groups that supply extra electron density to the electron-deficient B_{12} cores.[2,12] To our knowledge, however, dodecaborane clusters oxidized beyond the *hypercloso* state have never been reported. This redox boundary poses critical questions concerning the oxidation limit of icosahedral boron clusters, which is not only of fundamental interest, but could also have implications in the use of B_{12}-based materials for energy storage and other applications.[2,21–23]

As previously established,[2,12,20,21,24,25] the redox potential of alkoxy and benzyloxy-substituted B_{12} clusters ($[B_{12}(OR)_{12}]$) can be rationally tuned as a function of their substituents by greater than 1 V for the same redox event. With this in mind,

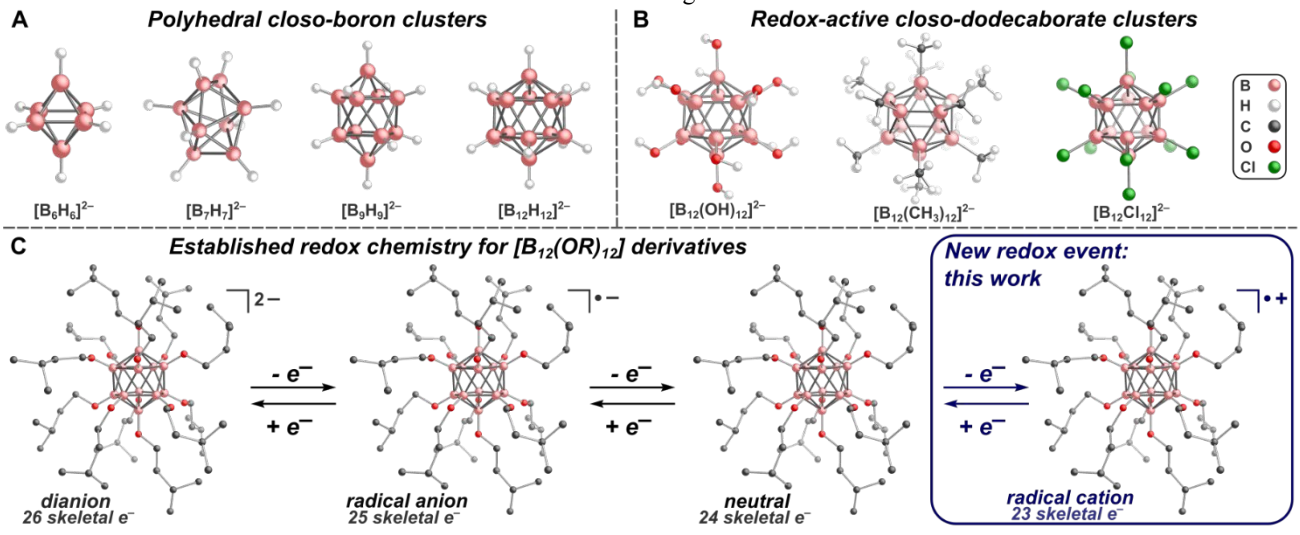


Figure 1. A: Structures of polyhedral *closo*-boron clusters as predicted by the Wade-Mingos electron-counting rules.[14,15] B: Examples of redox-active, perfunctionalized *closo*-dodecaborate clusters ($[B_{12}(OH)_{12}]^{2-}$,[19] $[B_{12}(CH_3)_{12}]^{2-}$,[18] and $[B_{12}Cl_{12}]^{2-}$[16]). C: Established redox chemistry for alkoxy and benzyloxy-substituted B_{12} clusters,[2,12,20,21,24,25] and this work, which introduces a third, reversible redox event for the B_{12}(O-3-methylbutyl)$_{12}$ (**1**) derivative.

stable and isolable monoanionic, *hypercloso*-$[B_{12}R_{12}]^{\bullet-}$, and in addition to the high chemical, electrochemical, and

structural stability of icosahedral boron clusters,[1,2,5,21,26–28] we envisioned we could tune and expand the redox potential window of $B_{12}(OR)_{12}$ derivatives through judicious selection of the supporting substituents. Surprisingly, during this work, we discovered a previously unrecognized electrochemical event that allowed us to observe the first example of a super-oxidized B_{12}-based radical cation at a chemically accessible potential (Figure 1C).

We identified the B_{12}(O-3-methylbutyl)$_{12}$ (**1**) derivative, originally reported by Hawthorne et al.,[12] as a model cluster for investigation due to the inherent steric protection provided by the bulky alkyl groups, which we predicted would provide extra stability to a highly reactive, cluster-based radical cation. Additionally, the inductive electron-donating nature of the 3-methylbutyl groups provides **1** with low potentials for the $[\mathbf{1}]^{2-/\bullet-}$ and $[\mathbf{1}]^{\bullet-/0}$ redox couples,[20] which we anticipated would shift a $[\mathbf{1}]^{0/\bullet+}$ couple to a potential accessible using common chemical oxidants. Here, we report the successful one-electron oxidation of *hypercloso*-**1**, yielding the $[\mathbf{1}]^{\bullet+}$ radical cation in isolable form. The super-oxidized $[\mathbf{1}]^{\bullet+}$ species introduces a new redox state of B_{12} clusters previously perceived as inaccessible, and represents the first characterized experimental example of a boron cluster-based three-electron violation of the Wade-Mingos rules.

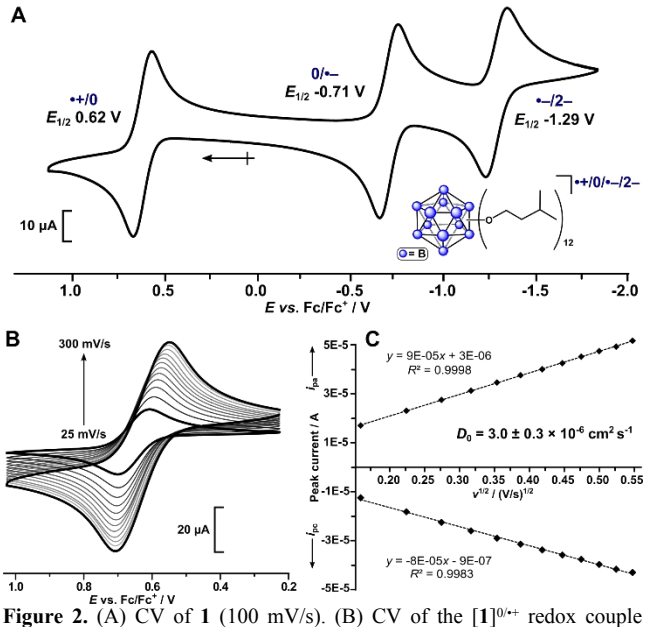
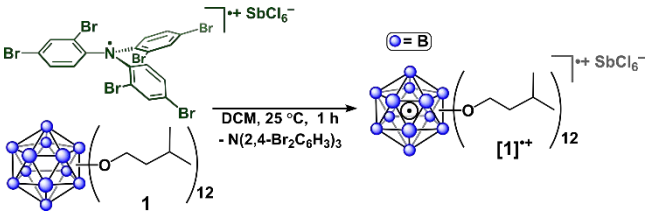


Figure 2. (A) CV of **1** (100 mV/s). (B) CV of the $[\mathbf{1}]^{0/\bullet+}$ redox couple recorded at variable scan rates. (C) Randles-Sevcik plot of the CV data from (B). A DCM solution of **1** (3 mM) with [^{n}Bu$_4$N][PF$_6$] (0.1 M) supporting electrolyte was used.

The **1** cluster was synthesized through per-*O*-alkylation of *closo*-$[B_{12}(OH)_{12}]^{2-}$ with 1-bromo-3-methylbutane followed by sequential two-electron chemical oxidation with $FeCl_3$•$6H_2O$.[12,24] Neutral, *hypercloso*-**1** was isolated in pure form as an air-stable solid, and was characterized by ^{1}H and ^{11}B NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS(+)), and UV–vis spectroscopy (SI Section S2.1).

We next evaluated the electrochemical properties of **1** by cyclic voltammetry (CV). The CV of **1** (Figure 2A) displays two reversible, one-electron redox events assigned to the $[\mathbf{1}]^{2-/\bullet-}$ (-1.29 V) and $[\mathbf{1}]^{\bullet-/0}$ (-0.71 V) couples (*vs.* Fc/Fc$^+$) with half-wave potentials ($E_{1/2}$) that are consistent with those previously reported.[20] However, anodic scanning past the $[\mathbf{1}]^{\bullet-/0}$ couple revealed a third reversible redox event at $E_{1/2}$ 0.62 V, which was not described in the original report.[20] We considered this electrochemical event could be attributed to the $[\mathbf{1}]^{0/\bullet+}$ couple, which is the first time to our knowledge that a 0/•+ B_{12}-based redox event has been observed for any dodecaborane cluster.

The scan rate dependent behavior of this new redox event indicated a diffusion-controlled reversible electrochemical process as judged by a Randles–Sevcik analysis[29] (Figure 2B, C) of peak current (i_p) *vs.* the square root of the scan rate ($\nu^{1/2}$). The diffusion coefficient (D_0) determined from this study was calculated as $3.0 \pm 0.3 \times 10^{-6}$ cm^2 s^{-1}, which is consistent with D_0 values reported for related $[B_{12}(OR)_{12}]$ clusters[21] and other molecular systems[30] of comparable size and shape.



Scheme 1. Protocol for the preparation of [**1**][SbCl$_6$].

The $[N(2,4\text{-}Br_2C_6H_3)_3]^{\bullet+}$ triarylaminium radical[31] was selected as a suitable reagent to effect the one-electron chemical oxidation of *hypercloso*-**1** due to its appropriate redox potential, ease of preparation, excellent stability, and convenience of handling.[32] Treatment of **1** with $[N(2,4\text{-}Br_2C_6H_3)_3][SbCl_6]$ in dichloromethane elicited a color change from dark yellow to yellow brown immediately upon addition (Scheme 1). After workup, the product of this reaction was analyzed by ^{1}H NMR spectroscopy (SI Figure S7), which revealed the formation of new and broadened resonances consistent with the generation of a paramagnetic species. In line with these data, the reaction product is silent by ^{11}B NMR spectroscopy (Figure 3A), which agrees well with the intended one-electron oxidation of the diamagnetic *hypercloso*-**1** cluster and formation of the paramagnetic $[\mathbf{1}]^{\bullet+}$ cation, and suggests the spin density is delocalized throughout the boron atoms of the cluster core.

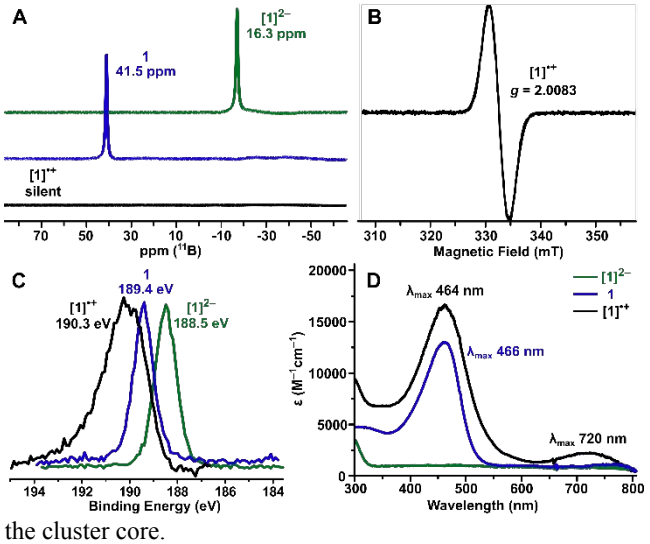


Figure 3. (A) ^{11}B{^{1}H} NMR spectra of $[Na(Et_2O)]_2$[**1**], **1**, and [**1**][SbCl$_6$]. (B) X-band CW-EPR spectrum of *in-situ* generated $[\mathbf{1}]^{\bullet+}$. (C) Boron 1*s* XPS data of $[Na(Et_2O)]_2$[**1**], **1**, and [**1**][SbCl$_6$]. (D) UV-vis spectra of $[Na(Et_2O)]_2$[**1**], **1**, and [**1**][SbCl$_6$].

Electron paramagnetic resonance (EPR) spectroscopy was used to further validate the paramagnetic nature of $[\mathbf{1}]^{\bullet+}$. The X-band continuous-wave (CW) EPR spectrum of *in-situ* generated $[\mathbf{1}]^{\bullet+}$ (Figure 3B) displays one relatively broad singlet centered at $g = 2.0083$ that is consistent with a doublet state. The broadness of this signal is due to extensive and overlapping hyperfine splitting patterns that result from the delocalization of a single electron across all twelve boron nuclei of the cluster core.[17,19] The signal broadness and isotropic *g*-factor of this species are consistent with EPR data of *hypocloso*-dodecaborate radical anion analogues that our group[23–25] and others[16–19] have previously reported, and further support the presence of an unpaired electron that is delocalized throughout the B_{12} core.

Before proceeding with the characterization of $[\mathbf{1}]^{\bullet+}$, we synthesized the *closo*-$[\mathbf{1}]^{2-}$ cluster for its use to benchmark the spectroscopic properties of 3-methylbutoxy-substituted clusters. *Closo*-$[\mathbf{1}]^{2-}$ was prepared through a two-electron chemical reduction of **1** with Na/Hg amalgam in Et_2O, and the $[Na(Et_2O)]_2[\mathbf{1}]$ salt was characterized by UV-vis spectroscopy, XPS, and heteronuclear NMR spectroscopy (^{1}H, ^{11}B). Efforts to isolate the *hypocloso*-$[\mathbf{1}]^{\bullet-}$ cluster in pure form unfortunately have thus far proven unsuccessful due to its rapid disproportionation to **1** and $[\mathbf{1}]^{2-}$ upon formation (SI Section S8).

X-ray photoelectron spectroscopy (XPS) has proven to be a valuable tool for assessing the charge state of molecular and extended network boron cluster systems based on predictable trends in boron 1*s* binding energies.[21,23–25] The XPS measurements of $[\mathbf{1}]^{\bullet+}$, **1**, and $[\mathbf{1}]^{2-}$ (Figure 3C) feature boron 1*s* regions that display the presence of intact molecular clusters with increasing binding energies that are consistent with the corresponding increased redox state of the clusters. The highest binding energy was observed for $[\mathbf{1}]^{\bullet+}$ (190.3 eV), and suggests that this cluster is the most oxidized of the series, further substantiating the electron-deficient nature of the B_{12} core, and our formulation of this species as a radical cation. The boron 1*s* binding energies observed for **1** and $[\mathbf{1}]^{2-}$ of 189.4 and 188.5 eV, respectively, agree well with the values reported for other *hypercloso* and *closo* cluster derivatives.[21,23–25]

As previously reported, sequential oxidation of colorless *closo*-$[B_{12}(OR)_{12}]^{2-}$ species to the *hypercloso* form leads to the formation of intensely colored solutions marked by diagnostic electronic absorption bands observed by UV-vis spectroscopy.[12,20,24,25] For the present system, the colorless $[Na(Et_2O)]_2[\mathbf{1}]$ salt displayed negligible absorptions across the visible region, while the UV-vis spectrum of **1** exhibits an absorption located at λ_{max} 466 nm that is attributed to charge transfer from the peripheral oxygen atoms of the alkoxy substituents to the B_{12} core.[2,12,24,25] The $[\mathbf{1}][SbCl_6]$ salt displays two major absorptions in the visible region at λ_{max} 464 and 720 nm (Figure 3D). Since the 720 nm absorption is a diagnostic feature of the radical cationic form, we performed time-dependent density functional theory (TD-DFT) calculations (*vide infra*) on the optimized geometry of $[\mathbf{1}]^{\bullet+}$ (SI Section S9.2) to investigate the electronic transitions that give rise to this defining absorption.

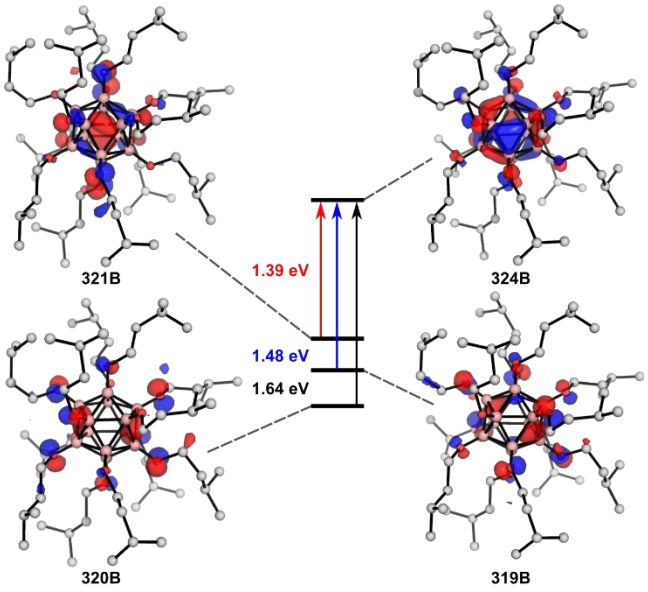
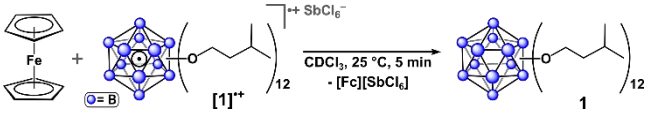


Figure 4. β-spin molecular orbitals of $[\mathbf{1}]^{\bullet+}$ involved in the transitions giving rise to the 720 nm absorption observed in the UV-vis spectrum (Figure 3D).

The TD-DFT calculations revealed that the 720 nm absorption is predominantly attributed to excitation of the β-spin electron from the occupied orbitals (MOs #319B, 320B, 321B) to the β-spin LUMO orbital (#324B) (Figure 4), which involve charge transfer from the peripheral oxygen atoms of the alkoxy substituents to the B_{12} cluster core. These results together with the spin density plot calculated for $[\mathbf{1}]^{\bullet+}$ (Figure S30) indicate that the unpaired electron is delocalized over both the electronegative oxygen atoms and the B_{12} cage.



Scheme 2. Protocol for the reduction of $[\mathbf{1}][SbCl_6]$ with ferrocene.

Having established the electrochemical reversibility of the $[\mathbf{1}]^{0/\bullet+}$ redox event, we next assessed its *chemical* reversibility through one-electron reduction of $[\mathbf{1}][SbCl_6]$ with ferrocene (Fc) (Scheme 2). Treatment of $[\mathbf{1}][SbCl_6]$ with ferrocene resulted in the rapid generation of **1** as assayed by ^{1}H and ^{11}B NMR spectroscopic analyses of the crude reaction mixture (SI Section S6). The clean chemical reversibility of this one-electron redox process is indicative that the B_{12}(O-3-methylbutyl)$_{12}$ architecture maintained its integrity during the course of the oxidation of **1** to $[\mathbf{1}]^{\bullet+}$ without suffering any deleterious processes such as degradation or loss of alkoxy substituents, and that the $[\mathbf{1}]^{\bullet+}$ species is in fact a well-defined and intact cluster.

This work presents the reversible electrochemical and chemical oxidation of *hypercloso*-**1**, to provide the first example of a super-oxidized, spin delocalized B_{12}-based radical cation whose identity was substantiated by various spectroscopic characterization. The discovery of $[\mathbf{1}]^{\bullet+}$ provides an entry point into a new class of stable B_{12} clusters that could potentially serve as extremely potent chemical oxidants, and whose reactivity has yet to be fully leveraged. The $[\mathbf{1}]^{\bullet+}$

species also poses interesting questions regarding the true oxidation limits of icosahedral boron clusters and contributes to a body of research interested in pushing the redox boundaries of archetypal molecular systems and the stabilization of unusual electronic states.[33–45]

ASSOCIATED CONTENT

The Supporting Information including experimental procedures and characterization data for all new compounds is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

Alexander M. Spokoyny *– Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Dr. E., Los Angeles, CA 90095; California NanoSystems Institute, University of California, Los Angeles 570 Westwood Plaza, Los Angeles, CA 90095*
orcid.org/0000-0002-5683-6240
Email: spokoyny@chem.ucla.edu
Thomas F. Miller III *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-4453-9716
Email: tfm@caltech.edu
Harry B. Gray *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-7937-7876
Email: hbgray@caltech.edu

Authors

Julia M. Stauber *– Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Dr. E., Los Angeles, CA 90095*
orcid.org/0000-0001-9783-907X
Josef Schwan *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
Xinglong Zhang *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0003-1698-692X
Jonathan C. Axtell[†] *– Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Dr. E., Los Angeles, CA 90095*
orcid.org/0000-0002-5579-4296
Dahee Jung *– Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Dr. E., Los Angeles, CA 90095*
orcid.org/0000-0003-1863-0193
Brendon J. McNicholas *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-3654-681X
Paul H. Oyala *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-8761-4667
Andrew J. Martinolich *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-7866-9594
Jay R. Winkler *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-4453-9716
Kimberly A. See *– Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125*
orcid.org/0000-0002-0133-9693

Present Addresses

†*The Dow Chemical Company, 633 Washington St., Midland, MI, 48674*

Notes

UCLA has patents on several compounds reported in this work from which A.M.S. and current/former co-workers may receive royalty payments. The $Cs_2[B_{12}(OH)_{12}]$ salt (Catalog #902209) is commercially available through the MilliporeSigma catalog.

ACKNOWLEDGMENT

This work was supported as part of the Center for Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award # DE-SC0019381 (A. M. S. and K. A. S. synthesis and characterization; T. F. M., computational work and theory). A. M. S. is a Research Corporation for Science Advancement (RCSA) Cottrell Scholar and a Dreyfus Foundation Camille Dreyfus Teacher-Scholar. Acknowledgment is made to the donors of The American Chemical Society Petroleum Research Fund for funding work in the H. B. G. lab (J.S. and H. B. G.). Work in the Beckman Institute at Caltech was supported by the Arnold and Mabel Beckman Foundation (B. J. M., J. R. W.). X. Z. acknowledges the Agency for Science, Technology and Research (Singapore) for an A*STAR fellowship. X. Z. and T. F. M. acknowledge the computational resources from the Extreme Science and Engineering Discovery Environment (XSEDE) Bridges computer at the Pittsburgh Supercomputing Center through allocation TG-MCB160013. A. J. M. acknowledges support through a postdoctoral fellowship from the Resnick Sustainability Institute at Caltech. D. J. acknowledges the UCLA Graduate Division for the Dissertation Year Fellowship. The National Science Foundation (NSF-1531940) and the Dow Next Generation Educator Fund are acknowledged for EPR facility support.

REFERENCES

(1) Hawthorne, M. F.; Pushechnikov, A. Polyhedral Borane Derivatives: Unique and Versatile Structural Motifs. *Pure Appl. Chem.* **2012**, *84* (11), 2279–2288.

(2) Axtell, J. C.; Saleh, L. M. A.; Qian, E. A.; Wixtrom, A. I.; Spokoyny, A. M. Synthesis and Applications of Perfunctionalized Boron Clusters. *Inorg. Chem.* **2018**, *57* (5), 2333–2350.

(3) Leśnikowski, Z. J. Challenges and Opportunities for the Application of Boron Clusters in Drug Design. *J. Med. Chem.* **2016**, *59* (17), 7738–7758.

(4) Dash, B. P.; Satapathy, R.; Maguire, J. A.; Hosmane, N. S. Polyhedral Boron Clusters in Materials Science. *New J. Chem.* **2011**, *35* (10), 1955–1972.

(5) Grimes, R. N. Boron Clusters Come of Age. *J. Chem. Educ.* **2004**, *81* (5), 657–672.

(6) Onak, T. Polyhedral Carbaboranes. *Comprehensive Organometallic Chemistry II* **1995**, 217–255.

(7) *Boron Science New Technologies and Applications*, 1st ed.; Hosmane, N. S., Ed.; Taylor & Francis Group, LLC: Boca Raton, 2012.

(8) *Handbook of Boron Science: With Applications in*

Organometallics, Catalysis, Materials and Medicine; Narayan S Hosmane, R. E., Ed.; World Scientific Publishing Europe Ltd.: London, 2019.

(9) Hosmane, N. S.; Maguire, J. A.; Yinghuai, Z. Polyhedral Boron Cage Compounds: An Account. *Main Group Chemistry* **2006**, *5* (4), 251–265.

(10) Polyhedral Carboranes. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier, 2007.

(11) Pitochelli, A. R.; Hawthorne, F. M. The Isolation of the Icosahedral B12H12-2 Ion. *J. Am. Chem. Soc.* **1960**, *82* (12), 3228–3229.

(12) Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. Synthesis of Stable Dodecaalkoxy Derivatives of Hypercloso-$B_{12}H_{12}$. *J. Am. Chem. Soc.* **2005**, *127* (51), 18243–18251.

(13) Wiersema, R. J.; Middaugh, R. L. Electrochemical Preparation and Halogenation of 1,1′-μ-Hydro-Bis(Undecahydro-Closo-Dodecaborate)(3-), $B_{24}H_{23}^{3-}$. *Inorg. Chem.* **1969**, *8* (10), 2074–2079.

(14) Wade, K. The Structural Significance of the Number of Skeletal Bonding Electron-Pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition-Metal Carbonyl Cluster Compounds. *J. Chem. Soc. D Chem. Commun.* **1971**, No. 15, 792–793.

(15) Mingos, D. M. P. Polyhedral Skeletal Electron Pair Approach. *Acc. Chem. Res.* **1984**, *17* (9), 311–319.

(16) Boeré, R. T.; Kacprzak, S.; Keßler, M.; Knapp, C.; Riebau, R.; Riedel, S.; Roemmele, T. L.; Rühle, M.; Scherer, H.; Weber, S. Oxidation of Closo-$[B_{12}Cl_{12}]^{2-}$ to the Radical Anion $[B_{12}Cl_{12}]^{\bullet-}$ and to Neutral $B_{12}Cl_{12}$. *Angew. Chem. Int. Ed.* **2011**, *50* (2), 549–552.

(17) Kaim, W.; Hosmane, N. S.; Záliš, S.; Maguire, J. A.; Lipscomb, W. N. Boron Atoms as Spin Carriers in Two- and Three-Dimensional Systems. *Angew. Chem. - Int. Ed.* **2009**, *48* (28), 5082–5091.

(18) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. An Unpaired Electron Incarcerated within an Icosahedral Borane Cage: Synthesis and Crystal Structure of the Blue, Air-Stable {[Closo-$B_{12}(CH_3)_{12}]^{\bullet}$}-Radical. *Chem. Commun.* **1999**, *12* (20), 2039–2040.

(19) Van, N.; Tiritiris, I.; Winter, R. F.; Sarkar, B.; Singh, P.; Duboc, C.; Muñoz-Castro, A.; Arratia-Pérez, R.; Kaim, W.; Schleid, T. Oxidative Perhydroxylation of $[Closo\text{-}B_{12}H_{12}]^{2-}$ to the Stable Inorganic Cluster Redox System $[B_{12}(OH)_{12}]^{2-/\bullet-}$: Experiment and Theory. *Chem. - A Eur. J.* **2010**, *16* (37), 11242–11245.

(20) Lee, M. W.; Farha, O. K.; Hawthorne, M. F.; Hansch, C. H. Alkoxy Derivatives of Dodecaborate: Discrete Nanomolecular Ions with Tunable Pseudometallic Properties. *Angew. Chem. - Int. Ed.* **2007**, *46* (17), 3018–3022.

(21) Barton, J. L.; Wixtrom, A. I.; Kowalski, J. A.; Qian, E. A.; Jung, D.; Brushett, F. R.; Spokoyny, A. M. Perfunctionalized Dodecaborate Clusters as Stable Metal-Free Active Materials for Charge Storage. *ACS Appl. Energy Mater.* **2019**, *2*, 4907–4913.

(22) Aubry, T. J.; Axtell, J. C.; Basile, V. M.; Winchell, K. J.; Lindemuth, J. R.; Porter, T. M.; Liu, J. Y.; Alexandrova, A. N.; Kubiak, C. P.; Tolbert, S. H.; Spokoyny, A. M.; Schwartz, B. J. Dodecaborane-Based Dopants Designed to Shield Anion Electrostatics Lead to Increased Carrier Mobility in a Doped Conjugated Polymer. *Adv. Mater.* **2019**, *31* (11), 1–8.

(23) Jung, D.; Saleh, L. M. A.; Berkson, Z. J.; El-Kady, M. F.; Hwang, J. Y.; Mohamed, N.; Wixtrom, A. I.; Titarenko, E.; Shao, Y.; McCarthy, K.; Guo, J.; Martini, I. B.; Kraemer, S.; Wegener, E. C.; Saint-Cricq, P.; Ruehle, B.; Langeslay, R. R.; Delferro, M.; Brosmer, J. L.; Hendon, C. H.; Gallagher-Jones, M.; Rodriguez, J.; Chapman, K. W.; Miller, J. T.; Duan, X.; Kaner, R. B.; Zink, J. I.; Chmelka, B. F.; Spokoyny, A. M. A Molecular Cross-Linking Approach for Hybrid Metal Oxides. *Nat. Mater.* **2018**, *17* (4), 341–348.

(24) Wixtrom, A. I.; Shao, Y.; Jung, D.; Machan, C. W.; Kevork, S. N.; Qian, E. A.; Axtell, J. C.; Khan, S. I.; Kubiak, C. P.; Spokoyny, A. M. Rapid Synthesis of Redox-Active Dodecaborane B12(OR)12 Clusters Under Ambient Conditions. *Inorg. Chem. Front.* **2016**, *3*, 711–717.

(25) Wixtrom, A. I.; Parvez, Z. A.; Savage, M. D.; Qian, E. A.; Jung, D.; Khan, S. I.; Rheingold, A. L.; Spokoyny, A. M. Tuning the Electrochemical Potential of Perfunctionalized Dodecaborate Clusters through Vertex Differentiation. *Chem. Commun.* **2018**, *54* (46), 5867–5870.

(26) Muetterties, E. L.; Balthis, J. H.; Chia, Y. T.; Knoth, W. H.; Miller, H. C. Chemistry of Boranes. VIII. Salts and Acids of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$. *Inorg. Chem.* **1964**, *3* (3), 444–451.

(27) Sivaev, I. B.; Bregadze, V. I.; Sjöberg, S. Chemistry of Closo-Dodecaborate Anion $[B_{12}H_{12}]^{2-}$: A Review. *Collect. Czechoslov. Chem. Commun.* **2002**, *67* (6), 679–727.

(28) Rupich, M. W. Characterization of Chloroclosoborane Acids as Electrolytes for Acid Fuel Cells. *J. Electrochem. Soc.* **1985**, *132* (1), 119–122.

(29) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley & Sons, 2001.

(30) McNicholas, B. J.; Grubbs, R. H.; Winkler, J. R.; Gray, H. B.; Despagnet-Ayoub, E. Tuning the Formal Potential of Ferrocyanide over a 2.1 V Range. *Chem. Sci.* **2019**, *10* (12), 3623–3626.

(31) Steckhan, E.; Schmidt, W. Elektrochemische Und Spektroskopische Untersuchung Bromsubstituierter Triarylamin-Redoxsysteme. *Chem. Ber.* **1980**, *113*, 577–585.

(32) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96* (2), 877–910.

(33) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. Dodecamethylcarba-Closo-Dodecaboranyl ($CB_{11}Me_{12}$), a Stable Free Radical. *J. Am. Chem. Soc.* **1996**, *118* (44), 10902–10903.

(34) King, B. T.; Michl, J. The Explosive "Inert" Anion $CB_{11}(CF_3)_{12}^-$. *J. Am. Chem. Soc.* **2000**, *122* (41), 10255–10256.

(35) Chiu, C. W.; Gabbaï, F. P. A 9-Borylated Acridinyl Radical. *Angew. Chem. - Int. Ed.* **2007**, *46* (10), 1723–1725.

(36) Liu, L.; Cao, L. L.; Shao, Y.; Ménard, G.; Stephan, D. W. A Radical Mechanism for Frustrated Lewis Pair Reactivity. *Chem* **2017**, *3* (2), 259–267.

(37) Eisenberg, R.; Gray, H. B. Noninnocence in Metal Complexes: A Dithiolene Dawn. *Inorg. Chem.* **2011**, *50* (20), 9741–9751.

(38) Malischewski, M.; Adelhardt, M.; Sutter, J.; Meyer, K.; Seppelt, K. Isolation and Structural and Electronic Characterization of Salts of the Decamethylferrocene Dication. *Science* **2016**, *353* (6300), 678–682.

(39) Evans, W. J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. *Organometallics* **2016**, *35* (18), 3088–3100.

(40) Soleilhavoup, M.; Bertrand, G. Cyclic (Alkyl)(Amino)Carbenes (CAACs): Stable Carbenes on the Rise. *Acc. Chem. Res.* **2015**, *48* (2), 256–266.

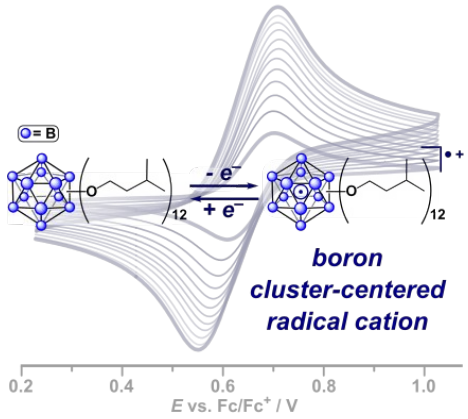
(41) Fisher, S. P.; Tomich, A. W.; Lovera, S. O.; Kleinsasser, J. F.; Guo, J.; Asay, M. J.; Nelson, H. M.; Lavallo, V. Nonclassical Applications of Closo-Carborane Anions: From Main Group Chemistry and Catalysis to Energy Storage. *Chem. Rev.* **2019**, *119*, 8262–8290.

(42) Wolczanski, P. T. Flipping the Oxidation State Formalism: Charge Distribution in Organometallic Complexes As Reported by Carbon Monoxide. *Organometallics* **2017**, *36* (3), 622–631.

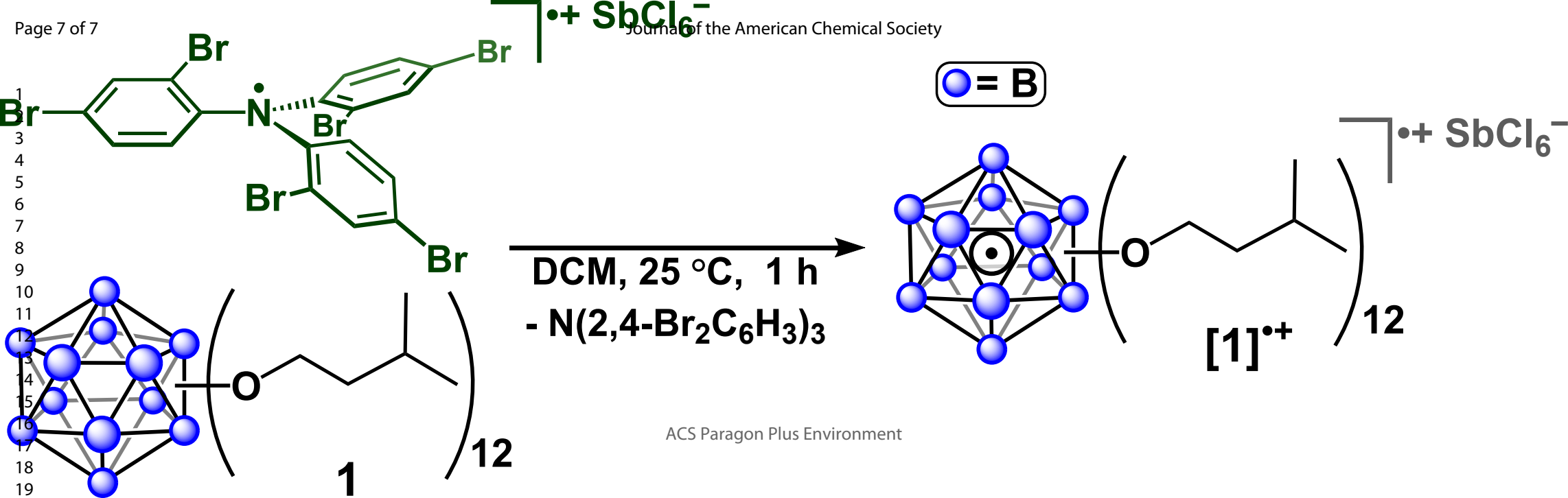
(43) Power, P. P. Persistent and Stable Radicals of the Heavier Main Group Elements and Related Species. *Chem. Rev.* **2003**, *103* (3), 789–809.

(44) Légaré, M. A.; Pranckevicius, C.; Braunschweig, H. Metallomimetic Chemistry of Boron. *Chem. Rev.* **2019**, *119*, 8231–8261.

(45) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. Carbene-Stabilized Main Group Radicals and Radical Ions. *Chem. Sci.* **2013**, *4* (8), 3020–3030.



For Table of Contents Entry Only


•+ SbCl6−
Br
Br
Br
Br
Br
N
O
12
1
DCM, 25 °C, 1 h
- N(2,4-Br2C6H3)3
= B
•+ SbCl6−
O
12
[1]•+